responses to individual papaya volatiles representative of the various fruit ripeness stages are also being recorded (D.M.L., E.B.J.). Details of these bioassay efforts will be published elsewhere.

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Factors Affecting the Thermal Degradation of *all-trans-β*-Carotene

Claire Marty[*] and Claudette Berset

Laboratoire Pigments Naturels et Couleur des Aliments, Département Science de l'Aliment, Ecole Nationale Supérieure des Industries Agricoles et Alimentaires, 1 Avenue des Olympiades, 91305 Massy, France

Thermal degradation compounds of *trans-β*-carotene were isolated by medium-pressure liquid chromatography and high-pressure liquid chromatography. The results of comparative tests on *trans-β*-carotene between a model system extrusion cooking process and heating at the same temperature were reported, and the effects of different medium conditions have been evaluated. Prolonged heating at 180 °C causes only limited breakdown of the molecule, but the presence of usual constituents of foods such as water or starch combined with mechanical mixing leads to much higher losses. The losses are increased by the presence of high pressure as is the case in extrusion cooking. Several hypotheses concerning the sequence of reactions involved in *trans-β*-carotene oxidative degradation are proposed.

Extrusion cooking is a widely used process in the food industry, and a variety of products are currently on the market, extensively developed at the level of organoleptic qualities (De la Guerivière et al., 1985). The color of

these products is one of the determining factors in consumer choice.

The extrusion cooking behavior of several carotenoid pigments, the most widely used in the food industry, has been reported (Lee et al., 1978; Kone and Berset, 1982; Berset et al., 1984; Berset and Marty, 1986). Thus, with the exception of the annatto, which is remarkably resistant to extrusion cooking, the stability of other commercial preparations of carotenoid pigments is judged by industry leaders to be insufficient.

Degradation begins in the extruder and continues during the several weeks of storage following treatment. The half-decoloration of the extrudates is reached between 100 and 200 days (Berset, 1987). The degradation of *all-trans-β*-carotene in extrusion cooking has been particularly investigated, and the main colored derivatives formed (β-carotene stereoisomers and epoxy, carbonyl, and hydroxyl derivatives) have been isolated and identified (Marty, 1986).

We report the results of comparative tests on *all-trans-β*-carotene, between a model system extrusion-cooking process and prolonged heating at the same temperature. The effects of factors such as the presence of starch and water and the result of permanent air circulation have been evaluated.

MATERIALS AND METHODS

The *all-trans-β*-carotene used in these tests was first purified from synthetic β-carotene (Fluka, purum grade) by chromatography on an alumina column (Marty and Berset, 1986a).

Extrusion Cooking (Treatment T1). Extrusion cooking tests were carried out with use of a BC 45 pilot machine (Clextral, 42701 Firminy, France) consisting of two copenetrating and corotating screws. Two tests involved 80 ppm *all-trans-β*-carotene and one involved 200 ppm, incorporated in native corn starch (Roquette Frères, 62136 Lestrem, France). The configuration of the corotary and copenetrating screws has been described recently (Marty and Berset, 1988). Experimental conditions: barrel temperature at the level of the last heating zone, 180 ± 2 °C; screw speed, 150 rpm; material flow rate, 25 kg/h; current, 23 A. Water was incorporated in the mixture at 2.4 L/h at the extruder inlet.

Heat Treatments. *Heating in Sealed Ampules (Treatment T2).* A 50-mg sample of *all-trans-β*-carotene dissolved in dichloromethane was added to a glass ampule. After the solvent was evaporated, the ampule was sealed and brought to 180 °C for 2 h. Four different ampules were similarly treated in each test.

Heating with Air Circulation (Treatment T3). A 200-mg portion of *all-trans-β*-carotene was added to a 25-mL flask. Air was blown into the flask with a pump so that the pigment was constantly swept during heating (2 h at 180 °C).

Heating with Air, Starch, and Water (Treatment T4). A mixture of 10 mg of *all*-trans-β-carotene, 50 g of starch, and 5 mL of distilled water was added to a 250-mL flask and the contents were stirred for 2 h at 180 °C. The proportions of the constituents were identical to those used in extrusion cooking. Each test was repeated three times. After heating, the samples were cooled and stored at -30 °C until chromatographic analysis.

Pigment Extraction. The pigments of the heated colorant-starch mixture (heating or extrusion cooking) were extracted with a binary mixture of n-hexane/acetone, 60/40 (v/v), after the enzymatic digestion of starch with α-amylase (Marty and Berset, 1986b). These operations are represented in Figure 1.

Chromatography on a Preparative Column. Preparative chromatography of the residual pigments after heat treatments was carried out on a column of activated alumina II-III (Merck, particle size 0.063-0.200 mm) (Figure 2). Fraction 1, eluted with n-hexane/diethyl ether, 90/10 (v/v), contained the stereoisomers of β-carotene. Fraction 2, eluted with n-hexane/diethyl ether, 40/60 (v/v), contained the epoxy and carbonyl derivatives of β-carotene.
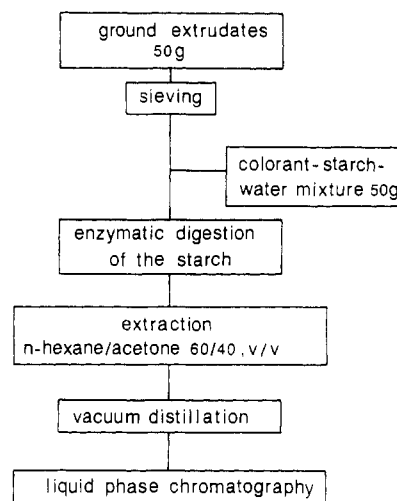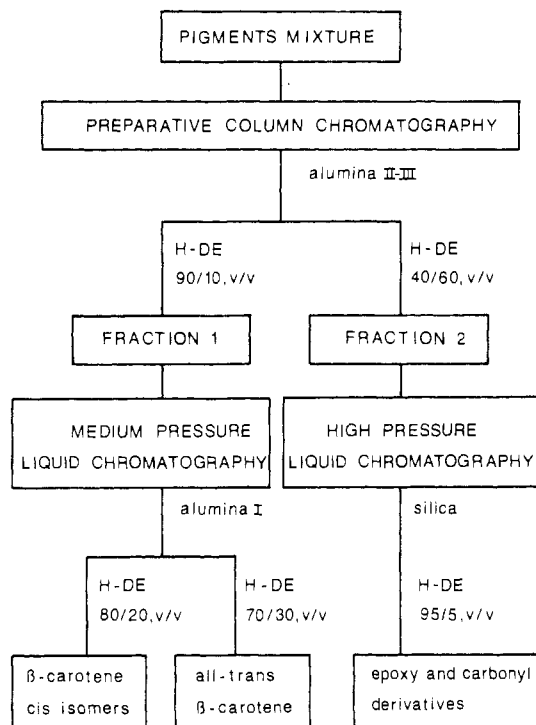

Figure 1. Diagram of pigment extraction.

Figure 2. Pigment fractionation by liquid-phase chromatography (H = n-hexane; DE = diethyl ether).

Medium-Pressure Liquid Chromatography. All the stereoisomers of β-carotene (fraction 1) were rechromatographed under medium pressure on a column of alumina 1 (Merck). This operation resulted in the isolation and quantification of residual *all-trans-β*-carotene (Figure 2). The setup used is described elsewhere (Marty and Berset, 1988). The quantity of residual *all-trans-β*-carotene was determined by spectrophotometry at 450 nm ($E_{1cm}^{1\%} = 2597$).

Separation of Oxidized Compounds by High-Performance Liquid Chromatography (HPLC). The HPLC fractionation of fraction 2 was carried out with a Gilson chromatograph (Gilson, 95400 Villiers le Bel, France) on a column of Lichrosorb Si 60 (Merck, 125 × 4 mm, 5 μm). Detection was with a Du Pont Model 8800 UV–visible detector operating at 420 nm. The elution system was n-hexane/diethyl ether, 95/5 (v/v), flow rate was 1 mL/min, pressure was 32 bars, and temperature was 22 °C.

The quantities of *all-trans-β*-carotene 5,6-epoxide, *all-trans-β*-carotene 5,8-epoxide, *all-trans-β*-apo-12′-carotenal, *all-trans-β*-apo-10′-carotenal, and *all-trans-β*-apo-8′-carotenal were determined after repeated injections and automatic peak collection. The extinction coefficients and wavelengths used, with corresponding references, are listed in Table I.

Table I. Extinction Coefficients and Wavelengths of Six Compounds in All-Trans Configuration

compound	$E_{1cm}^{1\%}$	solvent[a]	λ, nm	reference
β-carotene	2597	H	450	Marty and Berset (1986a)
β-carotene 5,6-epoxide	2670	H	446	Tsukida and Zechmeister (1958)
β-carotene 5,8-epoxide	2520	H	427	Tsukida and Zechmeister (1958)
β-apo-12′-carotenal	2160	PE	414	Ruegg et al. (1959)
β-apo-10′-carotenal	2190	PE	435	Ruegg et al. (1959)
β-apo-8′-carotenal	2640	PE	457	Ruegg et al. (1959)

[a] Key: H, *n*-hexane; PE, petroleum ether.

Table II. β-Carotene Stereoisomers Isolated after Extrusion Cooking (T1) and Heating in Sealed Ampules (T2)

compound	T1	T2
13,13′-di-*cis*-β-carotene	+	+
9,13′-di-*cis*-β-carotene	+	−
15-*cis*-β-carotene	+	−
13-*cis*-β-carotene	+	+
9,9′-di-*cis*-β-carotene	+	−
9-*cis*-β-carotene	+	+

RESULTS AND DISCUSSION

A total of 25 breakdown products of *all-trans-β*-carotene have thus far been isolated and identified after extrusion cooking (Marty and Berset, 1986b, 1988). They can be classified in six families: six mono- or polycis isomers of β-carotene, eleven mono- or diepoxy derivatives, five apocarotenals, one polyene ketone, one dihydroxyl derivative, and one monohydroxyl diepoxy derivative.

These compounds can be assayed only if the corresponding extinction coefficients are available. Only several have been published (Table I), and the small quantities produced in the tests made their determination impossible. As a first approximation for the comparison of the effects of different heat treatments, we determined the relative peak areas of each compound separated by HPLC. This could not be done for fraction 1 in the absence of an HPLC column adapted to fractionate β-carotene stereoisomers. In the case of this fraction, only a qualitative examination could be carried out.

Table II contains the structures of isomers isolated after heat treatments T1 and T2. It is seen that three of the six isomers appearing in the extrusion cooking were not detected after heating in sealed ampules. They are 9,13-di-*cis*-β-carotene, 15-*cis*-β-carotene, and 9,9′-di-*cis*-β-carotene. This would suggest that heating for 2 h at 180 °C in sealed ampules results in a more limited isomerization of *all-trans-β*-carotene than that occurring in extrusion cooking at the same temperature, an operation for which transit time in the extruder is not more than 1 min.

The chromatogram of the carbonyl and epoxy compounds formed after extrusion cooking is shown in Figure 3. The first unnumbered peak is a very small quantity of residual β-carotene carried over into fraction 2. Peaks numbered from 1 to 8 corresponded to monoepoxy derivatives (Marty, 1986). Their UV–visible spectral characteristics and configurations are reported in Table III. The positions of the cis double bonds could not be determined since the quantities of material required for nuclear magnetic resonance spectrometry are excessive. Table IV lists the relative peak areas of epoxy and carbonyl derivatives after the four different treatments.

Significant differences are noted when extrusion cooking (T1) is compared to heating in sealed ampules (T2). Derivatives containing a furanoid oxide function were present in lower quantities after treatment T2, and β-carotene 5,8:5′,8′-diepoxide was even undetectable. On the other hand, treatment T2 led to the appearance of a much larger proportion of slightly isomerized β-carotene
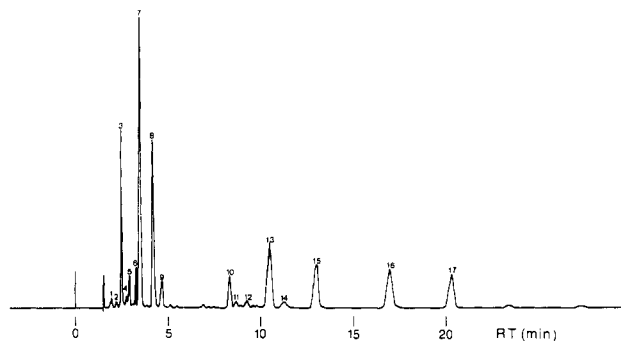

Figure 3. HPLC chromatogram of the carbonyl and epoxy compounds formed after extrusion cooking (RT = retention time).

Table III. Spectral Characteristics (Maxima in *n*-Hexane) and Configuration of β-Carotene 5,6-Epoxide and β-Carotene 5,8-Epoxide Stereoisomers[a]

compound	peak	maxima, nm		confign
β-carotene 5,6-epoxide	1	467.0, *440.0*, 422.8	330.9	cis
	2	472.8, *443.7*	331.1	cis
	3	474.2, *446.0*, 423.0		trans
β-carotene 5,8-epoxide	4	450.1, *423.8*	314.8	cis
	5	450.9, *425.1*	315.3	cis
	6	451.1, *425.9*, 403.0	315.5	cis
	7	452.6, *426.7*, 404.5		trans
	8	450.4, *425.1*, 404.4	315.0	cis

[a] The identification of these compounds has been previously determined (Marty and Berset, 1986b).

5,6-epoxide. According to El Tinay and Chichester (1970), the $C_5=C_6$ terminal double bond of the β-carotene molecule possesses the highest electron density. It would thus be a logical consequence that the epoxidation reaction occurs preferentially at this double bond ($C_5=C_6$ or $C_{5'}=C_{6'}$). Intermediate epoxides in position 5,6 would thus be generated before the rearrangement leading to the formation of the furanoid oxide ring in position 5,8. Heating in sealed ampules is a less brutal process, thus leading primarily to the first two steps in the reaction sequence, i.e. the formation of 5,6- and of 5,6′:5′,6′-epoxides (Marty and Berset, 1986b). When *all-trans-β*-carotene was heated in an open system with air circulation (T3), or in the presence of air, starch, and water in the same proportions as in the extruder mixture, the chromatographic profiles tended to resemble that of T1. There was thus a considerable decrease in the relative content of 5,6-epoxide derivatives and an increase in the relative content of 5,8-epoxide derivatives, notably the formation of β-carotene 5,8:5′,8′-diepoxide, the terminal product of the synthesis pathway for epoxy compounds according to our hypothesis. The presence of a continuous flow of air increases the encounter probability between β-carotene and oxygen as a result of turbulence created in the flask, thereby favoring the oxidation process. Starch and water, however, also play a role.

Figure 4 shows the positions of oxygen attack on the polyene chain of β-carotene, corresponding to the formation of five apocarotenals isolated after extrusion cooking and listed in Table IV.

Table IV. Relative Peak Areas of the β-Carotene Derivatives Formed after the Four Heat Treatments[a]

peak	compound	config	isomer	T1, %	T2, %	T3, %	T4, %
1	β-carotene 5,6-epoxide	cis	1	0.7	0.4	3.0	2.2
2		cis	2	0.7	0.4	2.4	2.5
3		trans	3	13.0	39.2	14.9	10.4
4	β-carotene 5,8-epoxide	cis	1	0.7	0.5	3.6	1.9
5		cis	2	1.6	0.8	3.2	2.8
6		cis	3	2.9	0.3	3.9	2.7
7		trans	4	21.3	22.5	29.0	22.9
8		cis	5	12.3	9.8	12.6	11.5
9	β-carotene 5,6:5′,6′-diepoxide	trans		2.6	6.4	3.0	1.0
10	β-carotene 5,6:5′,8′-diepoxide	trans		4.7		2.6	2.5
11	β-apo-15-carotenal	trans		0.8	1.0	1.5	1.1
12	β-apo-14′-carotenal	trans		1.1			0.8
13	β-carotene 5,8:5′,8′-diepoxide	trans		11.7		5.4	10.8
14	β-apo-12′-carotenal	trans		1.4		0.9	1.9
15	β-apo-8′-carotenal	trans		9.2	11.7	4.4	10.7
16	β-apo-10′-carotenal	trans		8.2	7.1	1.8	5.4
17	β-caroten-4-one	trans		7.4		7.8	8.8

[a] The identification of the compounds has been previously determined (Marty and Berset, 1986b, 1988).

β-apo-15-carotenal

β-apo-14′-carotenal

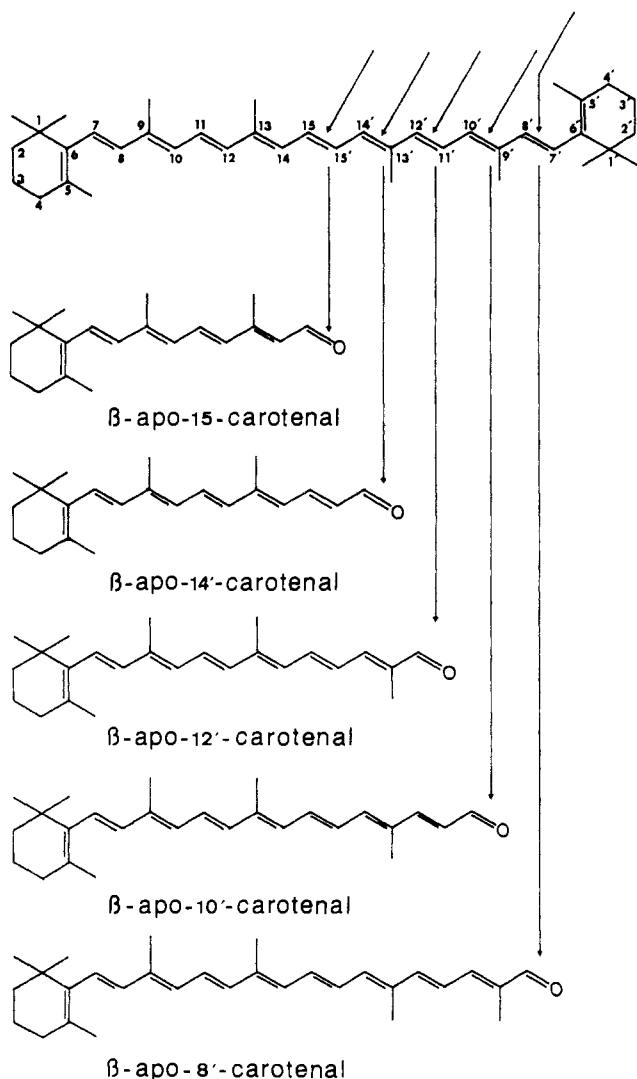β-apo-12′-carotenal

β-apo-10′-carotenal

β-apo-8′-carotenal

Figure 4. Positions of oxygen attack on the polyene chain of β-carotene corresponding to the formation of five apocarotenals isolated after extrusion cooking.

The relative proportions of apocarotenals as they appear in the table confirm a certain degree of gradation in the severity of heat treatments. β-Apo-14′-carotenal, β-apo-12′-carotenal, and β-caroten-4-one are not detected after treatment T2. On the other hand, these compounds do appear progressively when the composition of the medium approaches that of treatment T1.

This observation also enables us to propose a hypoth-

esis concerning the sequence of appearance of apocarotenals. Two series of arguments plead for a progressive shortening of the polyene chain two carbon atoms at a time:

Pullman (1960) reported that the C_7=C_8 bond had the highest mobility index (0.731) calculated with the molecular orbitals method. This would favor the progressive oxidative rupture of the C7=C8 double bond, leading to the formation of apo-8′-carotenal, a major compound formed in our heat treatments.

The lack of formation of β-apo-14′-carotenal and of β-apo-12′-carotenal after test T2 shows that in both cases only two oxidative breaks had occurred, leading to the formation of β-apo-8′- and β-apo-10′-carotenal. In treatment T3, the reaction is pushed to a further degree, with the appearance of β-apo-12′-carotenal and is complete in treatment T4, where β-apo-14′-carotenal can be detected.

Thus, chain breaks are recurrent and progress from the end of the molecule to the center. We can nonetheless not exclude the possibility of direct attack on all double bonds, in particular the central C_{15}=C_{15} bond, since β-apo-15-carotenal was detected after all four treatments. Oxidation of the polyene chain thus passes preferentially through a progressive shortening of the molecule without the possibility of forming apocarotenals by direct oxidation being null.

The oxidative break of a double bond in the β-carotene molecule leads to the formation of two carbonyl fragments of which one may be colorless. Thus, β-apo-8′-carotenal corresponds to β-cyclocitral; similarly, the formation of β-apo-10′-carotenal is accompanied by the disappearance of β-ionone, etc. These low molecular weight compounds were not investigated in the present work but were previously detected by other workers (Schreier et al., 1979; Ouyang et al., 1980).

Thus, our results added to other published data show that all the double bonds on the polyene chain of β-carotene can be oxidized in the course of a heat treatment. Only the formation of β-apo-11-carotenal has not yet been reported.

The comparative study of the four heat treatments would not be complete without a quantitative approach to the breakdown of β-carotene. We used the data listed in Table I to calculate the initial and residual quantities of all-trans-β-carotene, as well as those of all-trans-β-carotene 5,6-epoxide, all-trans-β-carotene 5,8-epoxide, all-trans-β-apo-12′-carotenal, all-trans-β-apo-10′-carotenal, and all-trans-β-apo-8′-carotenal. These compounds account for 53.1 and 80.5%, respectively, of the colored epoxy and carbonyl compounds formed during treatments T1

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Table V. Initial and Residual Quantities of *all-trans-β*-Carotene and Five Oxidative Degradation Compounds after Four Heat Treatments

compound	T1	T2	T3	T4
initial *all-trans-β*-carotene, mg	200	200	200	200
residual *all-trans-β*-carotene, mg	15	185	170	120
loss in *all-trans-β*-carotene, %	92	7.5	15	40
all-trans-β-carotene 5,6-epoxide, mg	2.52	0.41	0.36	0.64
all-trans-β-carotene 5,8-epoxide, mg	4.08	0.10	0.70	1.40
β-apo-12′-carotenal, mg	0.20		0.02	0.12
β-apo-10′-carotenal, mg	1.55	0.07	0.04	0.32
β-apo-8′-carotenal, mg	1.75	0.12	0.11	0.54
total of assayed degradn products, mg	10.1	0.70	1.23	3.02
assayed degradn compounds, %	5.5	4.7	4.1	3.8

and T2 (Table IV).

The results (Table V) show a considerable difference between the four heat treatments, extrusion cooking being by far the most destructive. The losses of *all-trans-β*-carotene are between 7.5 and 92%, depending on the treatment. It is also seen that the five breakdown products assayed here account for only 4–5% of the *all-trans-β*-carotene degraded. It is thus consistent to conclude that there is no accumulation of oxidized derivatives, since they are merely reaction intermediates of the thermal degradation of β-carotene. The volatile fraction not analyzed in this work is the largest fraction by weight, explaining why it was studied well before the appearance of modern analytical methods. Table V also shows that the five compounds assayed are found in proportions very close to the relative areas determined with HPLC and support the hypotheses proposed.

In addition, it seems evident that mixing by the oxygen in air and the presence of starch and water increase the intensity of the oxidation process, but these are not the only factors involved in the reactions occurring in the extruder cooker. The combined effects of pressure and shearing forces could cause an excessive temperature increase in the mixture during extrusion cooking. These conditions would explain the notable differences between prolonged heating in presence of air, starch and water (T4) and extrusion cooking.

CONCLUSIONS

The resistance of *all-trans-β*-carotene to high temperatures depends to a large extent on the conditions of the medium. Prolonged heating at 180 °C causes only limited breakdown of the molecule in the pure state, but the presence of usual constituents of foods, e.g., water or starch, combined with mechanical mixing favoring the diffusion of oxygen, can lead to much higher losses. These losses become maximal when the system energy is increased by the presence of high pressure, causing overheating as is the case in extrusion cooking.

We have proposed several hypotheses concerning the sequence of reactions involved in the oxidative degradation of the *all-trans-β*-carotene molecule. A kinetic study of the degradation will shed light on the mechanisms of formation of the oxidized derivatives and will lead to the determination of the place occupied by cis/trans isomerization in the thermal degradation sequences of β-carotene. Concerning nonoxidized volatile compounds, the degradation mechanisms proposed begin by the isomerization of the double bonds of *all-trans-β*-carotene (Hinnekens et al., 1976; Ishiwatari, 1980). In the case of the formation of oxidized derivatives, however, isomerization could occur in parallel with oxidation reactions, or else constitute an initial step destabilizing the molecule and favoring subsequent oxidative attacks. This hypoth-

esis implies the reversibility of cis/trans isomerization, since the oxidized derivatives isolated are all-trans.

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